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Measurements and predictions of outgassing from high density polyethylene (HDPE), PBX9502, and certain silicones by the isoconversional analysis

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ABSTRACT

The techniques of mass spectrometry and temperature programmed decomposition were used to measure outgassing kinetics from high density polyethylene, insensitive high explosive PBX 9502, and silica-filled polysiloxane TR55 and S5370. The isoconversional thermal analysis method was then employed to extract outgassing kinetics and to make kinetic predictions for long term outgassing at lower temperatures. The accuracy, advantages and disadvantages of the isoconversional analysis in terms of kinetic prediction for these materials and some others will be discussed.

INTRODUCTION

The outgassing from solid materials in vacuum devices may lead to compatibility issues and even undesirable effects on electronic components. In this article, the investigation on the outgassing species, the total amount of outgassing, and the outgassing kinetics of high density polyethylene (HDPE) in a vacuum environment at moderately elevated temperatures are reported. The long-term vacuum outgassing of HDPE at room temperature can be predicted based on the measured outgassing kinetics and the isoconversional thermal analysis method. Similar works on the moisture outgassing of the insensitive high explosive PBX9502, TR55 and S5370 silicones are also presented. Finally, effective outgassing mitigation technique as well as the suitability of the isoconversional analysis in terms of kinetic prediction for these materials and some others will be discussed.

EXPERIMENTAL

The main experimental technique to measure outgassing kinetics was temperature programmed decomposition/desorption (TPD). In all cases, either isothermal vacuum microbalance weight loss experiments or mass-spectrometer based outgassing were performed to compliment TPD kinetic data obtained in linear heating mode (1-3).

Kinetic parameters for the outgassing were obtained using Friedman's isoconversional analysis (4). The rate equation for a solid-state reaction can be approximated by:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) = \nu \cdot e^{-\frac{E}{RT}} \cdot f(\alpha) \quad (1)$$

where t is time; α is the reacted, desorption, outgassing, or decomposition fraction (0 to 1); k is the rate constant; ν is the pre-exponential factor which includes many constants describing the initial state of the sample such as three dimensional shape factors of initial particles, molecular mass, density, stoichiometry, active surface factors, number of lattice imperfections, and so forth; E is the activation energy for the rate controlling process; R is the gas molar constant, T is temperature in Kelvin; and $f(\alpha)$ is an analytical function determined by the rate-limiting reaction mechanism.

With a heating rate of $\beta = dT / dt$:

$$\frac{d\alpha}{dT} = \left[\frac{\nu}{\beta} \cdot f(\alpha) \right] \cdot e^{-\frac{E}{RT}} \quad (2)$$

Upon taking the natural logarithm on both sides of equation (1), the Friedman isoconversional analysis yields:

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln\{\nu f(\alpha)\} \quad (3)$$

A plot of $\ln(d\alpha/dt)$ vs. T^{-1} at some α value for a set of β values has the slope $-E/R$ (4). A plot of E vs. α is thus obtained by repeating the above procedure at other chosen α values between 0 and 1. This kinetic extraction procedure was first proposed by Friedman [4]. The susceptibility of the Friedman method to the blowing up of the term $\ln(d\alpha/dt)$ near the beginning/end of the reaction due to poor signal to noise ratio can be significantly reduced by increasing the data sampling frequency followed by data smoothing/averaging (1, 5).

Note that both E and $\{\nu f(\alpha)\}$ can be obtained the Friedman method based on equation (3). The time prediction, t_α , for a specific conversion α to be reached at the isothermal temperature T_o can be obtained from the rate equation (1) as following (1, 5):

$$t_\alpha = \int_0^{t_\alpha} dt = \int_0^\alpha \frac{d\alpha}{\{\nu f(\alpha)\} e^{-\frac{E}{RT_o}}} \quad (4)$$

Note that no assumption needs to be made about the pre-exponential factor ν or the rate limiting step $f(\alpha)$ in the isoconversional thermal analysis. As long as E and $\ln\{\nu f(\alpha)\}$ can be obtained from the slope and the intercept of the $\ln(d\alpha/dt)$ vs. $1/T$ plot, equation (4) can be employed to make kinetic prediction. The ability to make kinetic measurements and prediction without any prior knowledge of ν or $f(\alpha)$ is the strength of the isoconversional thermal analysis technique which is very suitable for kinetic problems involving unknown and complex processes with continually varying kinetic parameters (1, 5). Even in the case if the knowledge of the reaction is known in detail, the isoconversional thermal analysis can still serve to check on the kinetics derived from a model dependent analysis [5].

RESULTS AND DISCUSSION

Concerning HDPE, the majority of the outgassing species are $(C_2H_4)_n$ with $n = 1-4$ (2). Since all outgassing species evolve in unison with mass $(C_2H_4)_2$ as a function of temperature (2), the outgassing kinetics was extracted by analyzing the large TPD peak shift of just $(C_2H_4)_2$. The outgassing of the $(C_2H_4)_n$ species and the activation energy barrier for the outgassing are presented in Fig. 1(a) and (b), respectively.

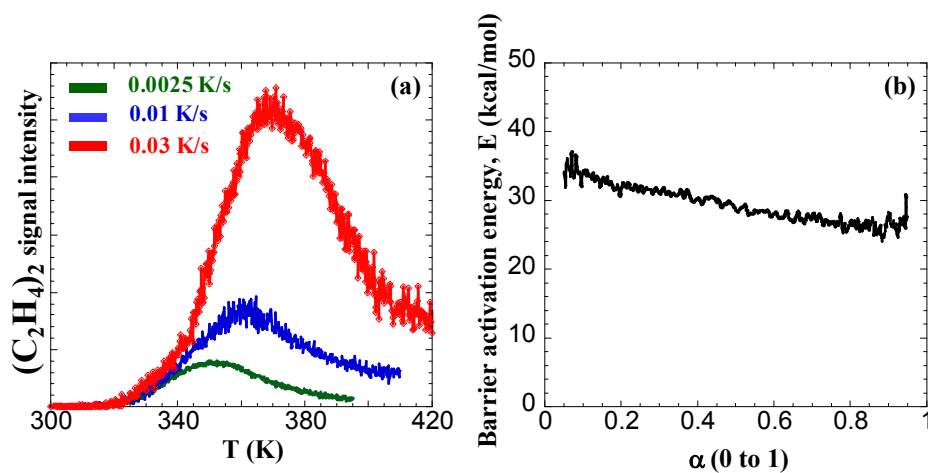


Fig. 1: TPD spectra of $(C_2H_4)_n$ at different heating rates (a) and the activation energy barrier obtained for the outgassing of $(C_2H_4)_n$ (b).

Due to a lack of proper calibration gases for the TPD results, quantitative kinetic prediction required the complimentary weight loss measurements of a vacuum microbalance. The weight losses of HDPE as measured by a vacuum microbalance at 323 K and 333 K are shown in Fig. 2(a) and (b).

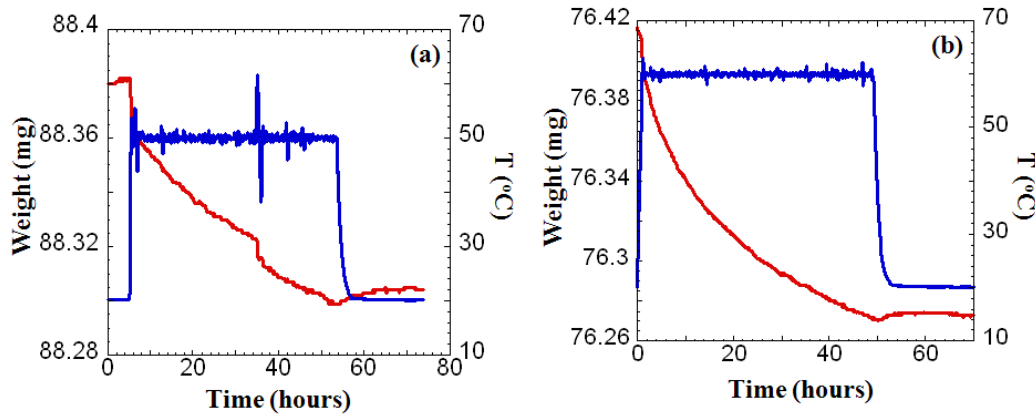


Fig. 2: The weight loss of HDPE as measured by a vacuum microbalance at 323 K (a) and 333K (b). The blue curves represent the temperature fluctuations during the isothermal experiments.

Isoconversional outgassing predictions are then matched with isothermal weight loss measurements from the vacuum microbalance to correlate between α and percentage of wt. loss. This is shown in Fig. 3(a) and (b). The experimental correlation between α and the percentage wt. loss is:

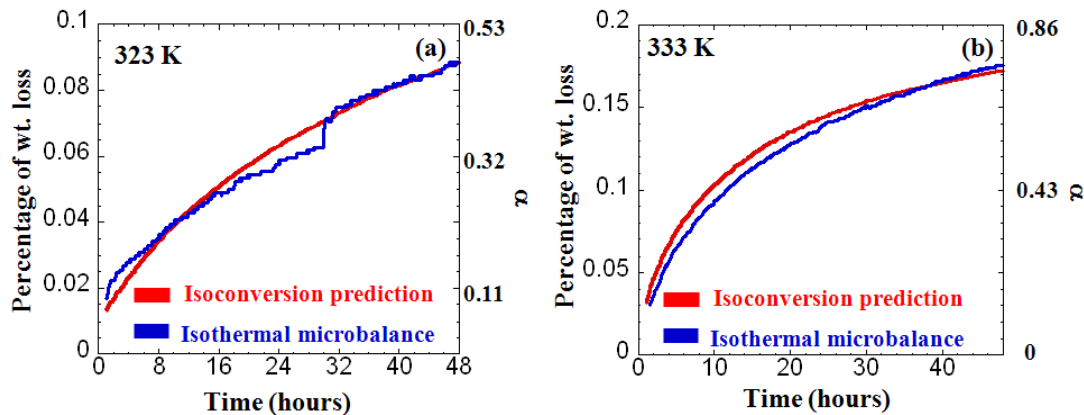
$$\text{Percentage wt. loss} = \alpha / (4.8 \pm 0.6) \quad (5)$$


Fig. 3: The matching of the actual weight loss of HDPE due to $(C_2H_4)_n$ outgassing as measured with a vacuum microbalance with outgassing models predicted by the isoconversional thermal analysis based on TPD data at 323 K (a) and 333 K (b).

Kinetic predictions of the outgassing from HDPE at room temperature and 343 K can be seen in Fig. 4(a) and (b). Clearly, most of the vacuum outgassing from HDPE takes place slowly over many years at room temperature. However, vacuum baking at elevated temperature prior to assembly will significantly reduce the potential outgassing.

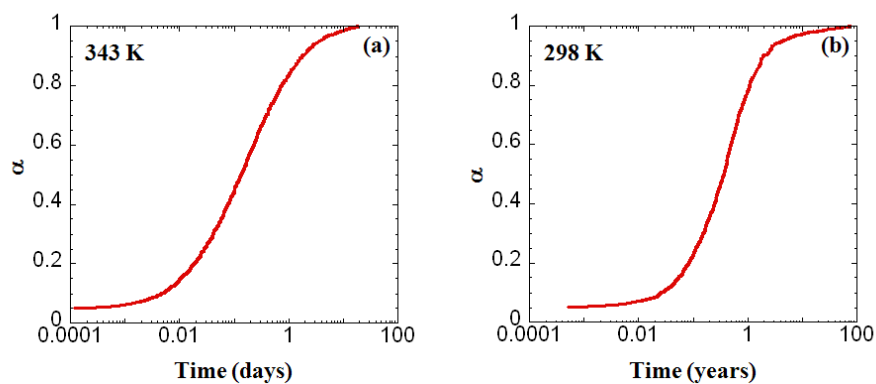


Fig. 4: Kinetic predictions of the outgassing from HDPE at 343 K (a) and 298 K (b).

By monitoring the atomic mass 18 with the mass-spectrometer in the TPD experiment setup and using similar analysis, kinetic measurements and predictions of moisture outgassing from PBX 9502 are presented in Fig. 5(a), (b), (c), and (d).

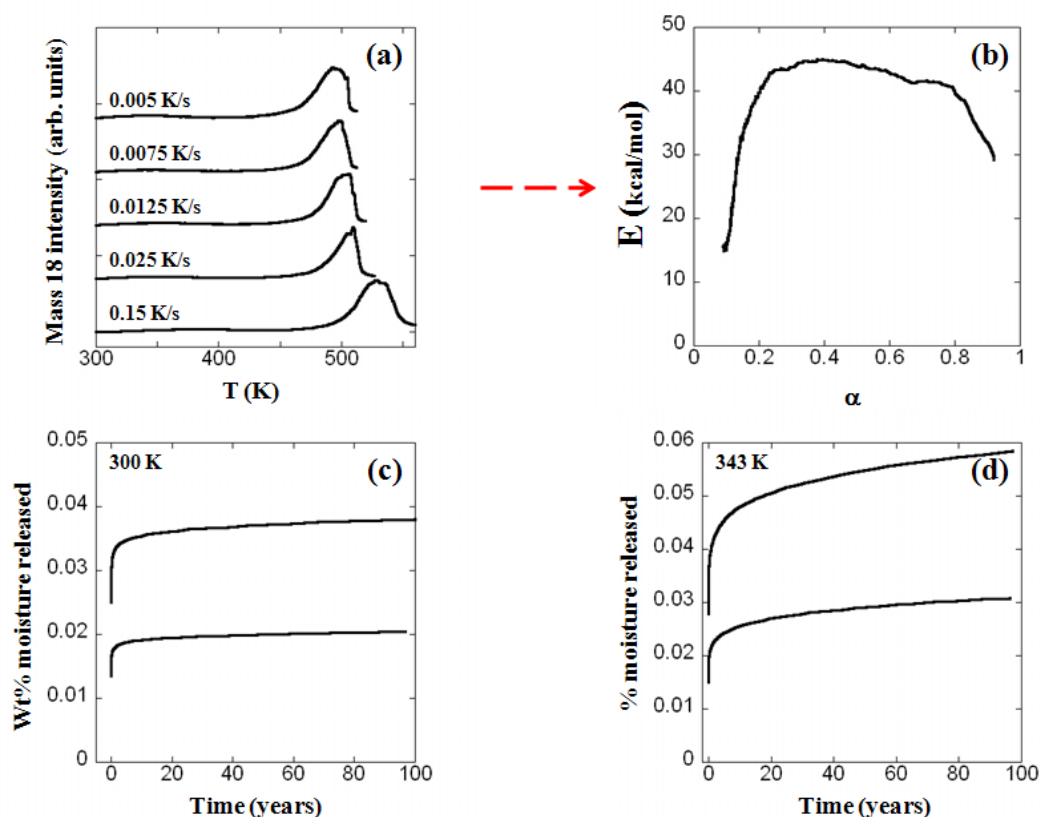


Fig. 5: (a) TPD spectra of moisture outgassing from PBX 9502 at different heating rates; (b) Activation energy barrier for moisture outgassing from PBX 9502; (c) Moisture outgassing prediction band at 300 K; (d) Moisture outgassing prediction at 343 K.

The level of agreement/discrepancy between isoconversional kinetic predictions and actual isothermal long-term outgassing from the works presented here can be observed from the comparison between actual isothermal moisture outgassing of S5370 and TR55 silicones at 313 K and 353 K and isoconversional predictions based on kinetics obtained from TPD data as shown in Fig. 6(a) and (b).

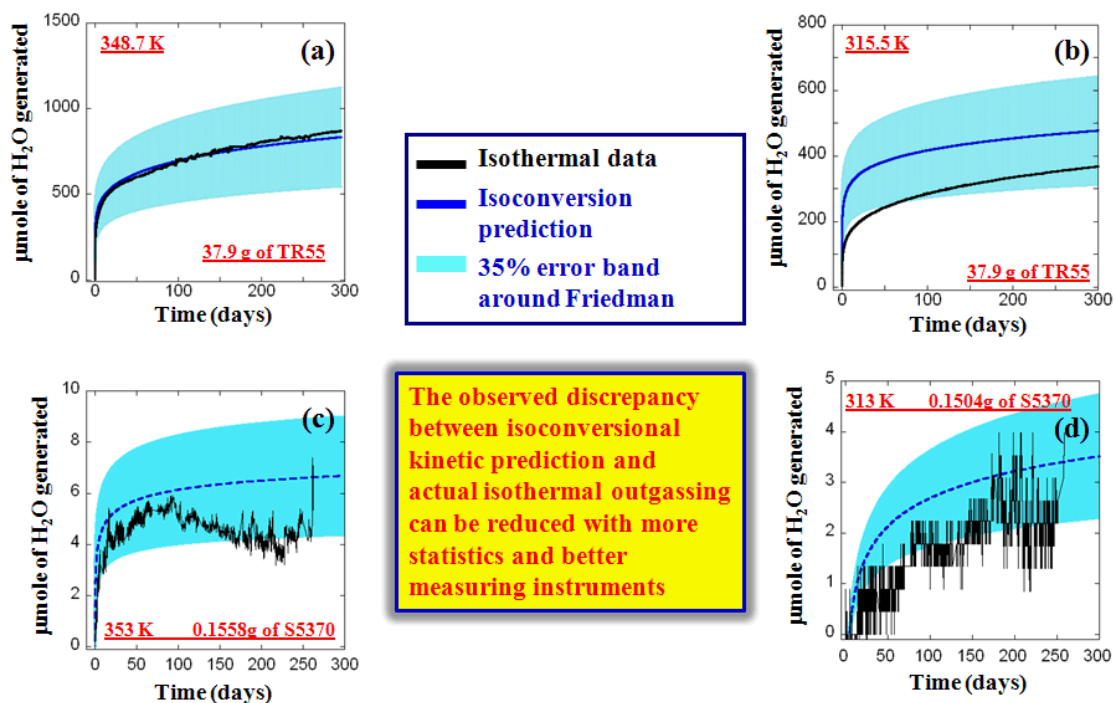


Fig. 6: Comparison of the level of agreement between isoconversional predictions and actual isothermal outgassing experiments on the moisture outgassing from TR55 (a and b) and S5370 (c and d).

In summary, the technique of isoconversional thermal analysis has been employed in the kinetic extraction and prediction of outgassing from a variety of solids: HDPE, PBX 9502, TR55 & S5370 silicones. The model-free predictions of outgassing based on the measured kinetics agree fairly well with actual isothermal outgassing. This agreement confirms the suitability of the isoconversional technique in the kinetic measurement and prediction of outgassing from many solids. However, complimentary techniques such as model-dependent thermal analysis at different heating rates should also be strongly encouraged in situations involving a strongly decreasing activation energy barrier, E , with increasing reacted fraction, α , as illustrated in Fig. 7 and discussed in detail in reference (5).

The isoconversional thermal analysis method fails functional self-consistency in region where E drops substantially with α

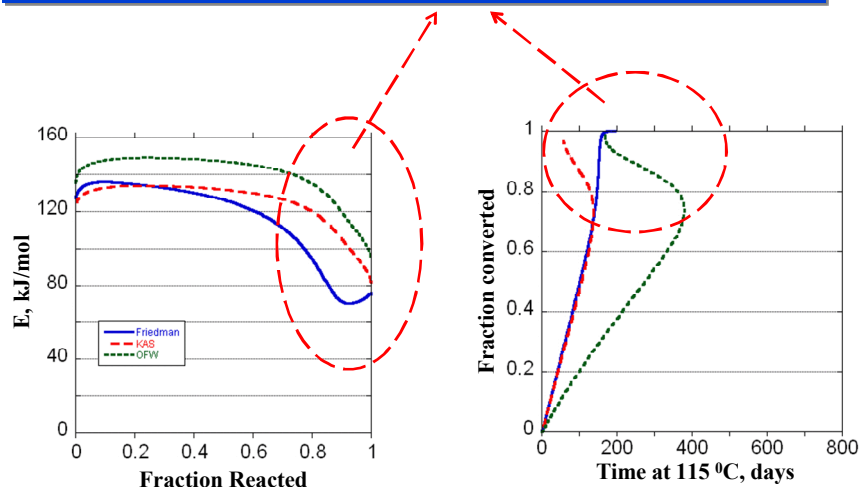


Fig. 7: An illustration of the failure of the isoconversional thermal analysis method in self-consistency in region where E drops substantially with α .

REFERENCES

1. L. N. Dinh, A. K. Burnham, M. A. Schildbach, R. A. Smith, R. S. Maxwell, B. Balazs, W. McLean II, *J. Vac. Sci. Technol. A*, 2007, 25, 597.
2. L. N. Dinh, J. Sze, M. A. Schildbach, S. C. Chinn, R. S. Maxwell, P. Raboin, W. McLean II, *J. Vac. Sci. Technol. A*, 2009, 27, 376.
3. L. N. Dinh, E. A. Glascoe, W. Small, *Lawrence Livermore National Laboratory technical report*, LLNL-TR-409894, 2009.
4. H. L. Friedman, *J. Polym. Sci., Part C: Polym. Symp.*, 1963, 6, 183.
5. A. K. Burnham, L. N. Dinh, *J. Therm. Anal. Cal.*, 2007, 89, 479.

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